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Structural, Optical, and Redox Properties of Lamellar Solids Derived from
Copper(I) Complexes and *n*-Butylammonium Uranyl Phosphate and Arsenate

by

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) A family of hydrated, layered solids has been prepared from intercalative ion-exchange reactions of <i>n</i> -butylammonium uranyl phosphate (BAUP) or arsenate (BAUAs), (<i>n</i> -C ₄ H ₉ NH ₃)-UO ₂ EO ₄ ·3H ₂ O (E = P, As), with Cu(LL) ₂ ⁺ complexes [LL is dmp = 2,9-dimethyl-1,10-phenanthroline; or bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline]. The products obtained were analyzed as having compositions [Cu(LL) ₂] _x [BA] _{1-x} UO ₂ EO ₄ ·2H ₂ O with <i>x</i> ≈ 0.2. X-ray powder diffraction data reveal that the compounds are single phases that can be indexed on the basis of a tetragonal unit cell. The solids exhibit absorption and photoluminescence (PL) properties characteristic of the Cu(LL) ₂ ⁺ species; the Cu(I) complexes completely quench the uranyl PL. Once intercalated, the Cu(I) complexes can be oxidized using Br ₂ vapor and re-reduced either photochemically or by N ₂ H ₄ vapor, as shown by changes in electronic and EPR spectra.			
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INTRODUCTION

Layered phosphates and arsenates are proving to be versatile host lattices for intercalative ion-exchange reactions.¹ We and others have shown that a variety of transition metal complexes can be intercalated into such hosts as α -Zr(HPO₄)₂ (ZrP), HUO₂PO₄·4H₂O (HUP), HUO₂AsO₄·4H₂O (HUAs), (*n*-C₄H₉NH₃)UO₂PO₄·3H₂O (BAUP), and (*n*-C₄H₉NH₃)UO₂AsO₄·3H₂O (BAUAs).²⁻⁹ The intercalants have participated in a variety of reactions, including excited-state energy transfer,² ligand photosubstitution,⁴ and acid-base/precipitation chemistry.⁵

An appealing set of candidate intercalants are Cu(I) complexes with bidentate ligands, Cu(LL)₂⁺. In particular, the room temperature photoluminescence (PL) and redox activity of the complexes Cu(dmp)₂⁺ and Cu(bcp)₂⁺ [dmp = 2,9-dimethyl-1,10-phenanthroline; bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline] have permitted extensive characterization of ground- and excited-state reactivity.¹⁰⁻¹⁶ We sought to determine how these properties would be influenced by incorporation of



the complexes into suitable lamellar host solids.

We report in this paper that single-phase, hydrated, lamellar solids of approximate composition $[\text{Cu}(\text{LL})_2]_x[\text{BA}]_{1-x}\text{UO}_2\text{EO}_4 \cdot 2\text{H}_2\text{O}$ ($\text{E} = \text{P}, \text{As}$; $x \sim 0.2$) can be prepared by intercalative ion-exchange reactions of the $\text{Cu}(\text{I})$ complexes with BAUP and BAUAs. Optical measurements reveal that while the photophysical properties of the $\text{Cu}(\text{I})$ complexes remain largely intact upon intercalation, strong host-guest interactions occur: the $\text{Cu}(\text{I})$ complexes quench the host UO_2^{2+} PL. We also demonstrate that the $\text{Cu}(\text{I})$ complexes undergo reversible redox chemistry within the lamellar structure that parallels their solution reactivity.

EXPERIMENTAL SECTION

Materials. Reagent grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was supplied by Matheson, Coleman, and Bell; 2,9-dimethyl-1,10-phenanthroline ("neocuproine"; 98%), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ("bathocuproine"; 99%), L-ascorbic acid (99%), and hydrazine monohydrate (98%) by Aldrich; reagent grade bromine by J. T. Baker; analytical grade $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_3PO_4 (85%) by Mallinckrodt; and As_2O_5 (99.9%) by Cerac. All materials

were used as received. A 1.0 M solution of H_3AsO_4 was prepared by dissolving 11.5 g As_2O_5 into 100 mL of boiling, triply-distilled water.

HUAs and HUP were prepared from uranyl nitrate and arsenic and phosphoric acid, respectively, as previously described.^{3,17} BAUAs and BAUP were prepared from reactions of *n*-butylamine with HUAs and HUP, respectively, as described previously.¹⁸

For the intercalants prepared below, Cu analyses were conducted by ICP emission spectroscopy using a Leeman Laboratories ICP 2.5 inductively-coupled plasma emission spectrophotometer. Compounds were dissolved in a minimum amount of concentrated HCl/HNO_3 , followed by dilution with de-ionized water. Standardized solutions for the ICP analyses were prepared by dissolving copper wire (Malin Company) in a minimum quantity of HNO_3 , followed by dilution with de-ionized water.

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) for determining hydration values employed a Netsch Geratebau STA 409 thermal analysis system. Typically, 50-mg samples were heated in air in alumina crucibles from 25°C to 500°C at 2.5°C/min.

$[\text{Cu}(\text{dmp})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{bcp})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$. These complexes were prepared using a slightly modified literature

preparation.¹⁹ In a typical synthesis, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in an acetate-buffered solution containing equal parts by volume of methanol, ethanol, and water. To this solution 2.2 equivalents of ligand and excess NaNO_3 were added. After addition of L-ascorbic acid to effect reduction, the solution was concentrated, yielding orange-red crystals. Products were recrystallized from an ethanol/water solution. Anal. Calcd. for $[\text{Cu}(\text{dmp})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$, $\text{C}_{28}\text{H}_{28}\text{N}_5\text{O}_5\text{Cu}$: Cu, 10.99. Found: Cu, 10.86. ϵ_{454} in $\text{CH}_2\text{Cl}_2 = 8,200 \text{ M}^{-1}\text{cm}^{-1}$. ^1H NMR (CD_2Cl_2): δ 8.52 (4H, d, $J_{\text{HH}} = 4\text{Hz}$), 8.05 (4H, s), 7.78 (4H, d, $J_{\text{HH}} = 4\text{Hz}$), 2.44 (12H, s). Anal. Calcd. for $[\text{Cu}(\text{bcp})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$, $\text{C}_{52}\text{H}_{44}\text{N}_5\text{O}_5\text{Cu}$: Cu, 7.20. Found: Cu, 7.58. ϵ_{477} in $\text{CH}_2\text{Cl}_2 = 13,700 \text{ M}^{-1}\text{cm}^{-1}$. ^1H NMR (CD_2Cl_2): δ 8.06 (4H, s), 7.77 (4H, s), 7.64 (20H, m), 2.58 (12H, s).

$[\text{Cu}(\text{dmp})_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$. This compound was prepared as described in the literature.²⁰ Anal. Calcd. for $\text{C}_{28}\text{H}_{28}\text{N}_6\text{O}_8\text{Cu}$: Cu, 9.93. Found: Cu, 10.47.

$[\text{Cu}(\text{LL})_2]_x[\text{BA}]_{1-x}\text{UO}_2\text{EO}_4 \cdot 2\text{H}_2\text{O}$ (LL = dmp, bcp; E = P, As; x ~0.2). In a representative reaction the Cu(I) complex was dissolved in a

1:1 ethanol/water mixture to make 125 mL of a ~20 mM solution and slurried in a 1.5:1 mole ratio with BAUP or BAUAs at 45°C for 3 days. The solution was filtered and washed with ethanol/water until the washings were colorless (usually 200 mL). The orange-red solid obtained was air-dried overnight and placed in a tightly sealed vial.

The Cu(I) loading level in the isolated compounds was determined by ICP and spectrophotometric analyses, the latter by dissolving the lattice in an acidified alcohol solution. Because of the low solubility of the copper complexes, a mixture of ethanol/water/HCl was required (1:1 ethanol/water mixture; pH of water/HCl before addition of ethanol = 2.6, as measured with a Corning Model 7 pH meter). The absorptivities of Cu(I) complexes in this medium were determined by preparing a series of physical mixtures of the Cu(I) complex and BAUP or BAUAs: for Cu(dmp)_2^+ , $\epsilon_{454} = 7,740 \text{ M}^{-1}\text{cm}^{-1}$ with BAUP and $7260 \text{ M}^{-1}\text{cm}^{-1}$ with BAUAs; for Cu(bcp)_2^+ , $\epsilon_{477} = 12,300 \text{ M}^{-1}\text{cm}^{-1}$ for either BAUP or BAUAs. The absorbances of these solutions were noted to decrease with time so that measurements were made as soon as dissolution was complete. The ICP analysis was performed as described above.

From thermogravimetric data, Cu analyses (ICP and

spectrophotometric) and elemental analyses (E&R Microanalytical Lab, Inc.) the approximate compositions of the solids of this study are: Anal.

Calcd. for $[\text{Cu}(\text{dmp})_2]_{0.22}[\text{BA}]_{0.78}\text{UO}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$: C, 19.75; H, 3.33; N, 4.12;

Cu, 2.48; U, 42.17; P, 5.49. Found: C, 23.21; H, 3.35; N, 4.30; Cu, 2.47; U,

39.50; P, 5.26. Anal. Calcd. for $[\text{Cu}(\text{dmp})_2]_{0.17}[\text{BA}]_{0.83}\text{UO}_2\text{AsO}_4 \cdot 2\text{H}_2\text{O}$: C,

16.50; H, 3.09; N, 3.59; Cu, 1.84; U, 40.47; As, 12.74. Found: C, 17.63; H,

2.89; N, 3.90; Cu, 1.90; U, 39.08; As, 12.71. Anal. Calcd. for

$[\text{Cu}(\text{bcp})_2]_{0.21}[\text{BA}]_{0.79}\text{UO}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$: C, 27.09; H, 3.53; N, 3.66; Cu, 2.14; U,

38.12; P, 4.96. Found: C, 28.26; H, 3.36; N, 3.93; Cu, 2.03; U, 36.85; P, 4.56.

Anal. Calcd. for $[\text{Cu}(\text{bcp})_2]_{0.18}[\text{BA}]_{0.82}\text{UO}_2\text{AsO}_4 \cdot 2\text{H}_2\text{O}$: C, 23.47; H, 3.28; N,

3.33; Cu, 1.77; U, 36.79; As, 11.58. Found: C, 24.50; H, 3.10; N, 3.45; Cu,

1.56; U, 35.97; As, 12.07. Solids were also analyzed for the presence of

ethanol by heating them to $\sim 65^\circ\text{C}$ at 10^{-5} torr and capturing the volatile

components in an NMR tube. The ^1H NMR spectrum (Bruker WP200SY)

revealed that no ethanol was present.

Structure. Powder X-ray diffraction data were collected on a Nicolet I2

rotating-stage powder diffractometer using $\text{Cu K}\alpha$ radiation; an internal Si

standard was employed. The patterns and cell constants were indexed and

refined by using least-squares analysis. Diffraction patterns were

indexed on the basis of tetragonal unit cells. Values of $1/d^2$ and hkl assignments based on a least-squares analysis are available as supplementary material. Infrared spectra were obtained on a Mattson Polaris NU-10000 FT-IR spectrophotometer using KBr pellets.

Optical Measurements. Electronic spectra were recorded on a Varian Cary 17-D UV-vis-near-IR spectrophotometer, using silicone grease mulls, as previously reported.³ PL spectra with 458-nm excitation were obtained using a Photon Technologies Inc. Model 01-150 high-intensity illumination system, which includes a Model 01-150X1 150-W Xe lamp, an elliptical mirror, and a Model 01-001 0.25-m monochromator. The PL signal was directed through a McPherson Model 270, 0.35-m monochromator and detected with a Hamamatsu R943-02 GaAs PMT. The PL intensity was obtained using a LeCroy Model 4604 photon counter, and data were collected using an Apple IIe microprocessor. Lifetimes were determined as described previously, using 450-nm excitation and a Hamamatsu R446 PMT for 690-nm detection of Cu(I) PL. Plots of log (intensity) vs. time were linear over at least 2 lifetimes. Quantum yields were determined as previously described.³

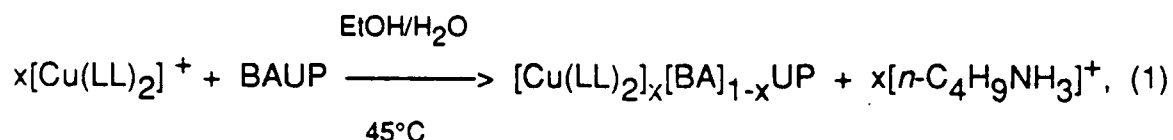
Redox Chemistry. Bromine vapor was used to effect oxidation of the Cu(I)-intercalated solids. In a typical reaction 25-50 mg of

$[\text{Cu}(\text{dmp})_2]_{0.22}[\text{BA}]_{0.78}\text{UO}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were placed in a 450-mL closed vessel containing ~5 mL of Br_2 . The sample was fully oxidized within a few minutes, as determined by visible spectroscopy. Chemical reduction of the oxidized sample with N_2H_4 vapor was accomplished in a similar manner and was completed after ~45 min, as determined by visible and EPR spectroscopies. EPR spectra were obtained from solid samples using a Varian E-15 spectrometer. An internal cell-within-a-cell DPPH standard was used to calibrate the signal. Photochemical reduction of the oxidized sample was carried out using the 468-nm line of a Coherent Innova Kr^+ laser ($\sim 350 \text{ mW/cm}^2$); reduction was usually detected after ~30 min.

RESULTS AND DISCUSSION

A family of powdered samples, $[\text{Cu}(\text{LL})_2]_x[\text{BA}]_{1-x}\text{UO}_2\text{EO}_4 \cdot 2\text{H}_2\text{O}$ (LL is dmp = 2,9-dimethyl-1,10-phenanthroline; or bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; BA = (*n*- $\text{C}_4\text{H}_9\text{NH}_3$); E = P, As; $x \sim 0.2$), have been prepared and characterized. In sections below, we describe the synthesis and composition, structural, optical, and redox properties of these materials.

Synthesis and Composition. The $[\text{Cu}(\text{LL})_2]_x[\text{BA}]_{1-x}\text{UO}_2\text{EO}_4 \cdot 2\text{H}_2\text{O}$ solids can be prepared by the intercalative ion-exchange reaction shown below,



wherein the Cu(I) complex exchanges with some of the *n*-butylammonium cations within the uranyl phosphate, BAUP, or arsenate, BAUAs, hosts. The use of an ethanol/water mixture at elevated temperatures improves the solubility of the Cu(I) precursor and leads to a single-phase product. Occasionally, solids with *x* as large as ~0.4 have been isolated, but *x* ~0.2 is typical. Efforts to intercalate the complexes under analogous conditions using HUP or HUAs as precursors were unsuccessful, presumably due to the large size of the guest ion.

In many respects the physicochemical properties of the four solids of this study (dmp or bcp ligands bonded to Cu(I) with phosphate or arsenate host lattices) are sufficiently similar that data collected for $[\text{Cu}(\text{dmp})_2]_{0.22}[\text{BA}]_{0.78}\text{UO}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, CudmpUP, can be regarded as illustrative.

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were performed to assess hydration. Shown in Figure 1 are

typical TGA and DTA traces for CudmpUP, which reveal that the air-dried solid is approximately a dihydrate. The precipitous drop in the TGA at temperatures greater than $\sim 250^{\circ}\text{C}$ is likely due to decomposition of the Cu(I) complex, the nitrate salt of which decomposes at $\sim 260^{\circ}\text{C}$.²¹ Decomposition would mask loss of additional water, so the hydrate values given should be treated as lower limits. Given our synthetic conditions, we were concerned that ethanol might have been incorporated into the solids,²² but the volatile products collected upon heating the compounds *in vacuo* showed no evidence of the alcohol by ^1H NMR spectroscopy.

Structure. All of the isolated solids were single phases, based on powder X-ray diffraction data that are summarized in Table I. The X-ray data indicate the Cu(I)-intercalated materials to be lamellar solids whose powder patterns, like those of the BAUP^{3,23} and BAUAs precursors, can be indexed in tetragonal symmetry. Shown in Figure 2 are X-ray powder diffraction patterns of CudmpUP and the starting material, BAUP.

The Table I data indicate that the a lattice parameter is insensitive to the presence of the Cu(I) complex and reflects the choice of phosphate or arsenate host lattice. However, after intercalation of the Cu(I) complex, there is generally a $\sim 1\text{-}5\text{ \AA}$ increase in the interlamellar

spacing, $c/2$. The choice of ligand appears to influence the interlamellar spacing, with the more sterically demanding bcp causing greater lattice expansion than dmp. It is noteworthy that the addition of triply-distilled water to these air-dried powders causes an additional $\sim 3\text{-}4$ Å increase in the interlamellar spacing, as shown in Table I, and reduces sample crystallinity. Allowing the compounds to dry in air restores the original powder pattern within a few minutes. No attempt was made to quantify the amount of additional water taken up by the lattice.

Retention of the original lamellar structure in the intercalated compounds was further confirmed by the phosphate infrared stretching frequencies. The peaks located at $\sim 1120\text{ cm}^{-1}$ and $\sim 1000\text{ cm}^{-1}$ have been assigned to the phosphate stretching modes in HUP,^{24,25} while the peak at $\sim 810\text{ cm}^{-1}$ has been assigned to the arsenate stretching mode in HUAs.^{26,27} These stretching frequencies are retained in the intercalated solids, as illustrated in Figure 3 for CudmpUP and CudmpUAs. Figure 3 also shows that the IR spectra of the intercalated solids appear to be the sum of the uranyl phosphate (arsenate) bands and the characteristic $[\text{Cu}(\text{dmp})_2][\text{NO}_3]\cdot 2\text{H}_2\text{O}$ bands.

Optical Properties. The $\text{Cu}(\text{dmp})_2^+$ - and $\text{Cu}(\text{bcp})_2^+$ -intercalated

compounds are orange-red and red, respectively. Figure 4 shows that the color for the $\text{Cu}(\text{dmp})_2^+$ -intercalated compounds derives from an intense band with $\lambda_{\text{max}} \sim 460 \text{ nm}$ that is present in the absorption spectrum of $[\text{Cu}(\text{dmp})_2][\text{NO}_3] \cdot 2\text{H}_2\text{O}$ and assigned as a metal-to-ligand charge transfer (MLCT) transition.^{28,29} The absence of the structured absorption due to UO_2^{2+} that is present in the accompanying BAUP spectrum is a consequence of the roughly thousand-fold greater absorptivity of the $\text{Cu}(\text{I})$ complex.

All of the $\text{Cu}(\text{I})$ -loaded solids showed room temperature PL characteristic of the $\text{Cu}(\text{I})$ complex.¹² Figure 5 compares the uncorrected PL of $\text{Cu}(\text{dmp})_2\text{UP}$ with a concentration-matched (1:4 mole ratio) physical mixture of $[\text{Cu}(\text{dmp})_2][\text{NO}_3] \cdot 2\text{H}_2\text{O}$ and BAUP, at 295 and 77K. The characteristic $\text{Cu}(\text{I})$ PL bands at 690 and 730 nm are evident at both temperatures. This $\text{Cu}(\text{I})$ PL has been investigated in detail by McMillin et al. and described as two excited states of MLCT origin in thermal equilibrium.¹² The other solids display similar features, indicating that intercalation does not drastically alter the excited-state manifold of the $\text{Cu}(\text{I})$ complex.

Additional support for this notion comes from photophysical

measurements of the Cu(I)-intercalated compounds. Table II presents lifetimes τ and radiative quantum yields ϕ_r of the intercalated solids and solid-state and solution data for the Cu(I) nitrate salts. Corresponding unimolecular rate constants for radiative and nonradiative decay were calculated using eqs. 2 and 3 and are also given in Table II. In general,

$$k_r = \phi_r / \tau \quad (2)$$

$$k_{nr} = (1/\tau) - k_r \quad (3)$$

the Cu(I) PL is inefficient and short-lived. The values shown in Table II for the Cu(I)-intercalated solids are intermediate between the solid-state and solution values,¹² as might be expected.

A more substantive effect resulting from intercalation is the complete quenching of host UO_2^{2+} PL between 500 and 600 nm, as revealed by the physical mixture/intercalated-solid comparison of Figure 5. Because BAUP is only weakly emissive at 295 K, this effect is much more pronounced at 77K, where BAUP rivals HUP in emissive efficiency.³ While some contribution to quenching may arise from the trivial mechanism (absorption of UO_2^{2+} PL by the Cu(I) complex), the comparisons of Figure 5 argue that the Cu(I) complex quenches the UO_2^{2+} PL by excited-state

energy and/or electron transfer: in the former case, the Cu(I) complexes possess low-lying MLCT excited states;¹⁹ in the latter case they are oxidizable by excited UO_2^{2+} .^{13,16} All of the other Cu(I)-intercalated guests caused similar quenching of UO_2^{2+} PL at 295 and 77K.

Oxidation. It is well established that Cu(dmp)_2^+ can be oxidized to Cu(dmp)_2^{2+} .^{11,19} We wanted to ascertain whether similar chemistry obtains in the layered host. Oxidation using Br_2 vapor was successful: the compounds rapidly changed from an orange-red to a green color. A comparison of the electronic spectrum of the oxidized compound with an aqueous solution of Cu(dmp)_2^{2+} is shown in Figure 6. After exposure to Br_2 , the characteristic Cu(I) MLCT band is no longer present in the visible spectrum of the oxidized species, but the characteristic weak d-d transitions of the $\text{Cu}^{2+} \text{d}^9$ system can be seen in the near-IR region. That the oxidized layered solid's spectrum does not exactly match that of Cu(dmp)_2^{2+} likely reflects different cation environments. Further evidence that the Cu(dmp)_2^+ has been oxidized is shown by the EPR trace

of Figure 7. The $\text{Cu}(\text{dmp})_2^+$ compound is converted from an EPR-silent d^{10} system to an EPR-active d^9 system.

The insensitivity of the IR phosphate stretching region to the oxidation reaction provides evidence that the gross integrity of the $\text{Cu}(\text{dmp})\text{UP}$ lamellar structure is preserved. However, considerable loss of crystallinity was evident from X-ray powder diffraction patterns of the oxidized solids, which were sufficiently poor that indexing was not possible.

Exposing the newly-oxidized, $\text{Cu}(\text{II})$ -intercalated compound to N_2H_4 vapor caused reduction of the complex back to $\text{Cu}(\text{I})$, as judged by loss of the EPR signal and the return of the characteristic $\text{Cu}(\text{dmp})_2^+$ MLCT absorption band (slightly shifted to $\lambda_{\text{max}} \sim 440 \text{ nm}$) and PL properties. Moreover, the IR spectrum revealed no loss of the lamellar structure. The $\text{Cu}(\text{II})$ -intercalated solid could alternatively be photochemically reduced with exposure to 468-nm light. The mechanism that has been proposed for the photoreduction involves the homolytic cleavage of a copper(II)—water bond in an acidic medium, yielding H^+ , OH^\cdot , and $\text{Cu}(\text{I})$.³⁰ Complete photoreduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ was not achieved in solution nor were we able to accomplish this in the layered solid.³⁰ No attempt was made to

isolate the products of the photoreduction.

Interestingly, efforts to intercalate Cu(II) directly into BAUP or BAUAs using $[\text{Cu}(\text{dmp})_2][\text{NO}_3]_2$ were unsuccessful. The resulting materials were either contaminated with $[\text{Cu}(\text{dmp})_2]^+$ or consisted of multiple phases. Attempts to intercalate first dmp and then Cu^{2+} were unsuccessful: A single-phase, dmp-intercalated solid was prepared, but intercalation with Cu^{2+} yielded only $\text{Cu}_{0.5}\text{UP}$ as shown by X-ray powder diffraction patterns.³¹

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Table I. Lattice Parameters^a

Compound	a (Å)	$\frac{1}{2} c^b$ (Å)
[Cu(dmp) ₂] _{0.22} [BA] _{0.78} UP·2H ₂ O Fully Hydrated ^{c, d}	6.974 (5) -----	16.99 (7) -----
[Cu(dmp) ₂] _{0.17} [BA] _{0.83} UAs·2H ₂ O Fully Hydrated ^c	7.179 (2) 7.31 (2)	16.83 (3) 19.54 (6)
[Cu(bcp) ₂] _{0.21} [BA] _{0.79} UP·2H ₂ O Fully Hydrated ^c	7.009 (3) 6.976 (3)	19.99 (3) 22.87 (2)
[Cu(bcp) ₂] _{0.18} [BA] _{0.82} UAs·2H ₂ O Fully Hydrated ^c	7.207 (3) 7.259 (8)	19.51 (4) 23.48 (7)
BAUP	6.987 (5)	14.61 (1)
BAUAs	7.183 (9)	15.48 (2)

^a All samples were single phases that could be indexed to tetragonal unit cells. Errors in table entries are estimated standard deviations based on least-squares refinement. ^b The $c/2$ lattice parameter represents the interlamellar spacing, viz., the interplanar spacing between adjacent uranyl phosphate layers.³² ^c A fully hydrated sample is obtained by adding triply-distilled water directly onto the sample. ^d The fully hydrated CudmpUP yielded two phases.

Table II. Emissive Properties^a

Compound	τ^b (ns)	$10^4\phi_f^c$	$10^{-3}k_r^d(\text{s}^{-1})$	$10^{-6}k_{nr}^e(\text{s}^{-1})$
$[\text{Cu}(\text{dmp})_2]_{0.22}[\text{BA}]_{0.78}\text{UP}\cdot 2\text{H}_2\text{O}$	140	5.6	4.0	7.1
$[\text{Cu}(\text{dmp})_2]_{0.17}[\text{BA}]_{0.83}\text{UAs}\cdot 2\text{H}_2\text{O}$	92	5.5	6.0	11
$[\text{Cu}(\text{bcp})_2]_{0.21}[\text{BA}]_{0.79}\text{UP}\cdot 2\text{H}_2\text{O}$	220	6.1	2.8	4.5
$[\text{Cu}(\text{bcp})_2]_{0.18}[\text{BA}]_{0.82}\text{UAs}\cdot 2\text{H}_2\text{O}$	150	5.9	3.9	6.7
$[\text{Cu}(\text{dmp})_2][\text{NO}_3]\cdot 2\text{H}_2\text{O}^f$	320	16	5.0	3.1
$[\text{Cu}(\text{bcp})_2][\text{NO}_3]\cdot 2\text{H}_2\text{O}^f$	380	34	8.9	2.6
$\text{Cu}(\text{dmp})_2^{+g}$	90	2.1	2.3	11
$\text{Cu}(\text{bcp})_2^{+g}$	80	2.5	3.1	12

^a Emissive data were obtained at 295K. ^b Lifetimes were obtained with 450-nm excitation, as described in the Experimental Section. ^c The radiative quantum efficiencies were obtained with 450-nm excitation, as described in the Experimental Section. Errors in the radiative quantum efficiencies have been estimated to be $\pm 25\%$.³³ ^d Unimolecular radiative rate constants were calculated using Equation 2 in the text.

^e Unimolecular nonradiative rate constants were calculated using Equation 3 in the text. ^f Emissive properties were obtained from solid samples.

^g The $[\text{Cu}(\text{dmp})_2]\text{BF}_4$ and $[\text{Cu}(\text{bcp})_2]\text{PF}_6$ salts were dissolved in CH_2Cl_2 at 25°C. Data taken from ref. 12.

Figure 1. TGA and DTA data for CudmpUP.

Figure 2. X-ray powder diffraction patterns for CudmpUP and the starting material, BAUP. The internal silicon standard is denoted by an asterisk (*).

Figure 3. Infrared spectra of $[\text{Cu}(\text{dmp})_2][\text{NO}_3] \cdot 2\text{H}_2\text{O}$ (A), CudmpUP (B), and CudmpUAs (C). Spectra were obtained from KBr pellets at room temperature.

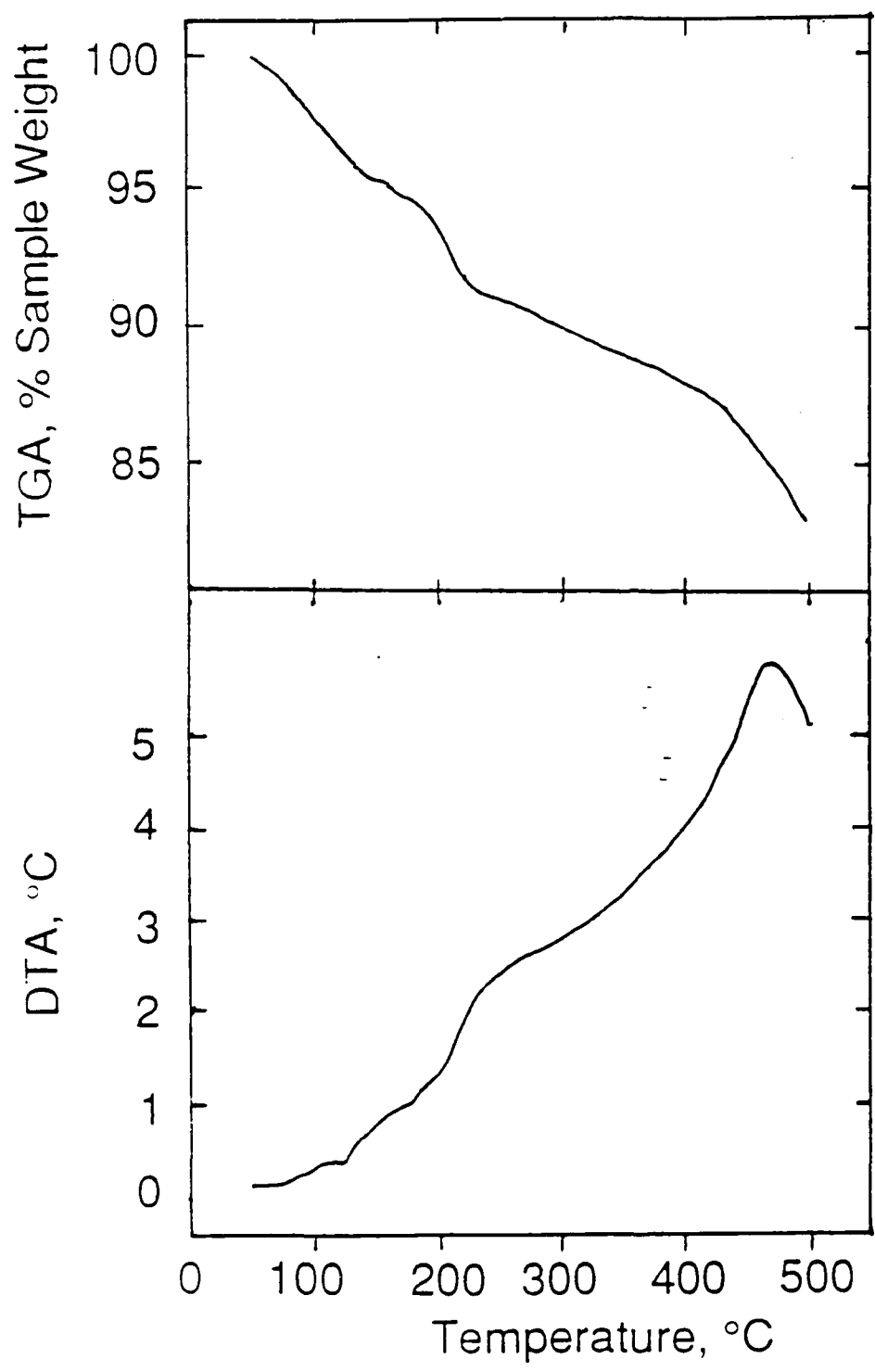
Figure 4. Visible absorption spectra (295K). Left panel : $\text{Cu}(\text{dmp})_2^+$ in CH_2Cl_2 (—) and BAUP (-----). Right panel : CudmpUP (—). The solid samples were prepared as silicone grease mulls on filter paper.

Figure 5. Uncorrected PL spectra for CudmpUP (—) and a concentration-matched physical mixture of BAUP and $[\text{Cu}(\text{dmp})_2][\text{NO}_3] \cdot 2\text{H}_2\text{O}$ (•••••). Spectra in the upper panel were obtained at room temperature and those in the lower panel at 77K. Spectra were normalized to a common maximum intensity. The samples were excited at 458 nm.

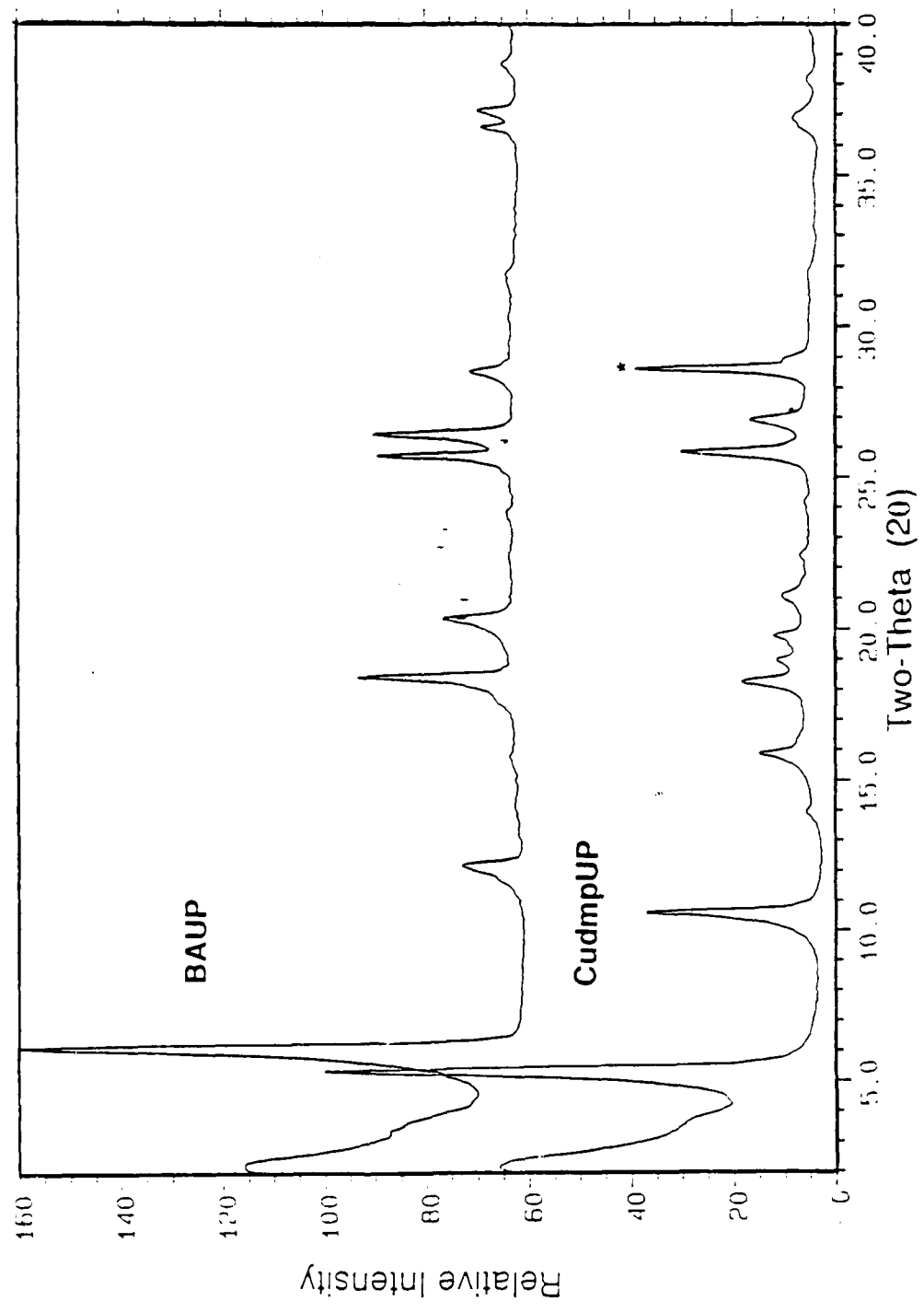
Figure 6. Visible absorption spectra of CudmpUP before oxidation (A; -----) and after oxidation by Br_2 (B; —). Spectrum C (•—•—•) is that of $\text{Cu}(\text{dmp})_2^{2+}$, obtained in water after dissolution of the nitrate salt. Spectra A and B were prepared as silicone grease mulls on filter paper.

Figure 7. The EPR spectra of solid CudmpUP (A), after oxidation with Br_2 (B), and after reduction with N_2H_4 (C). The DPPH calibration peak is denoted with an asterisk (*).

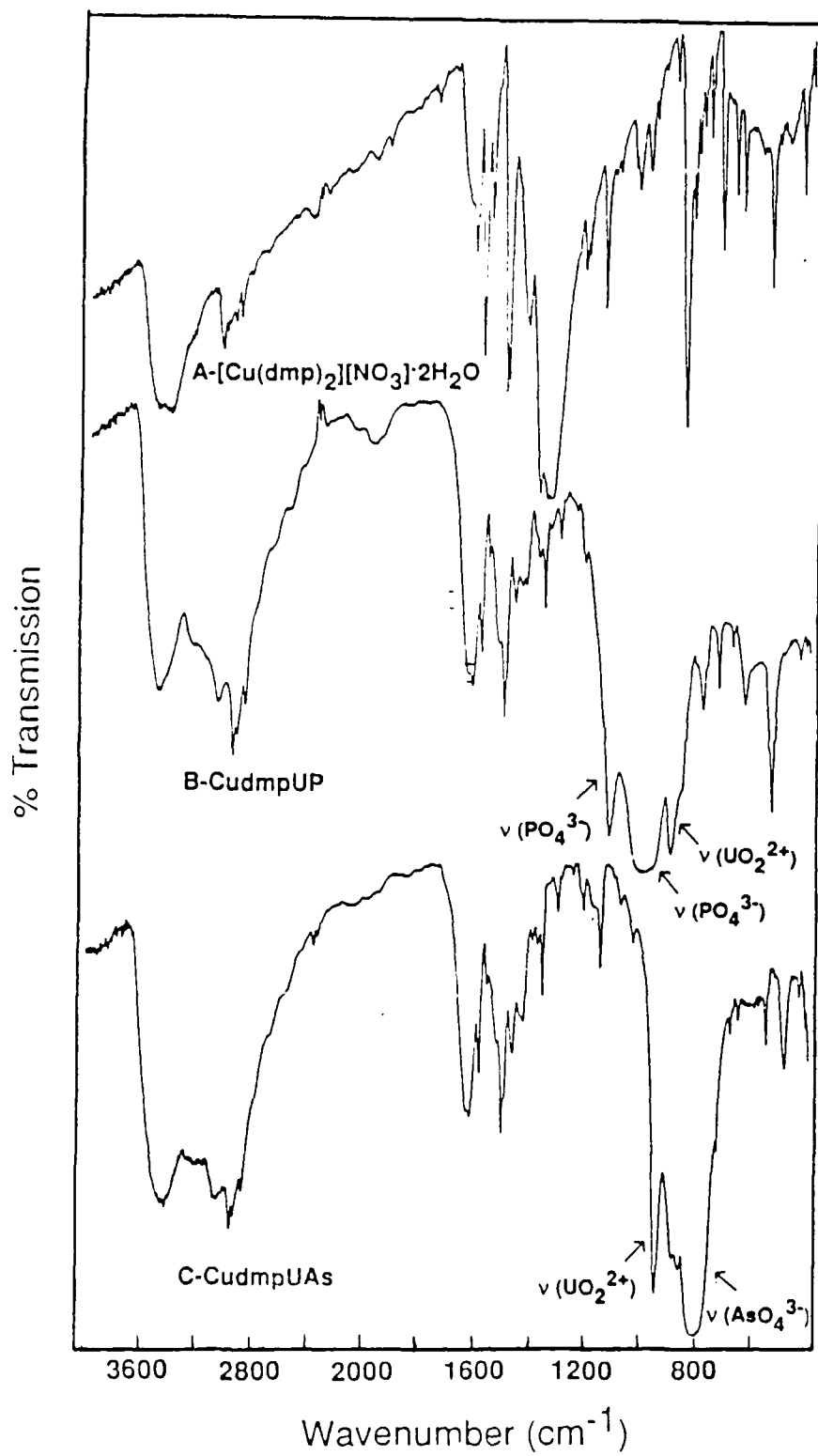
Fig 1



F, 2



F-3



F. 4

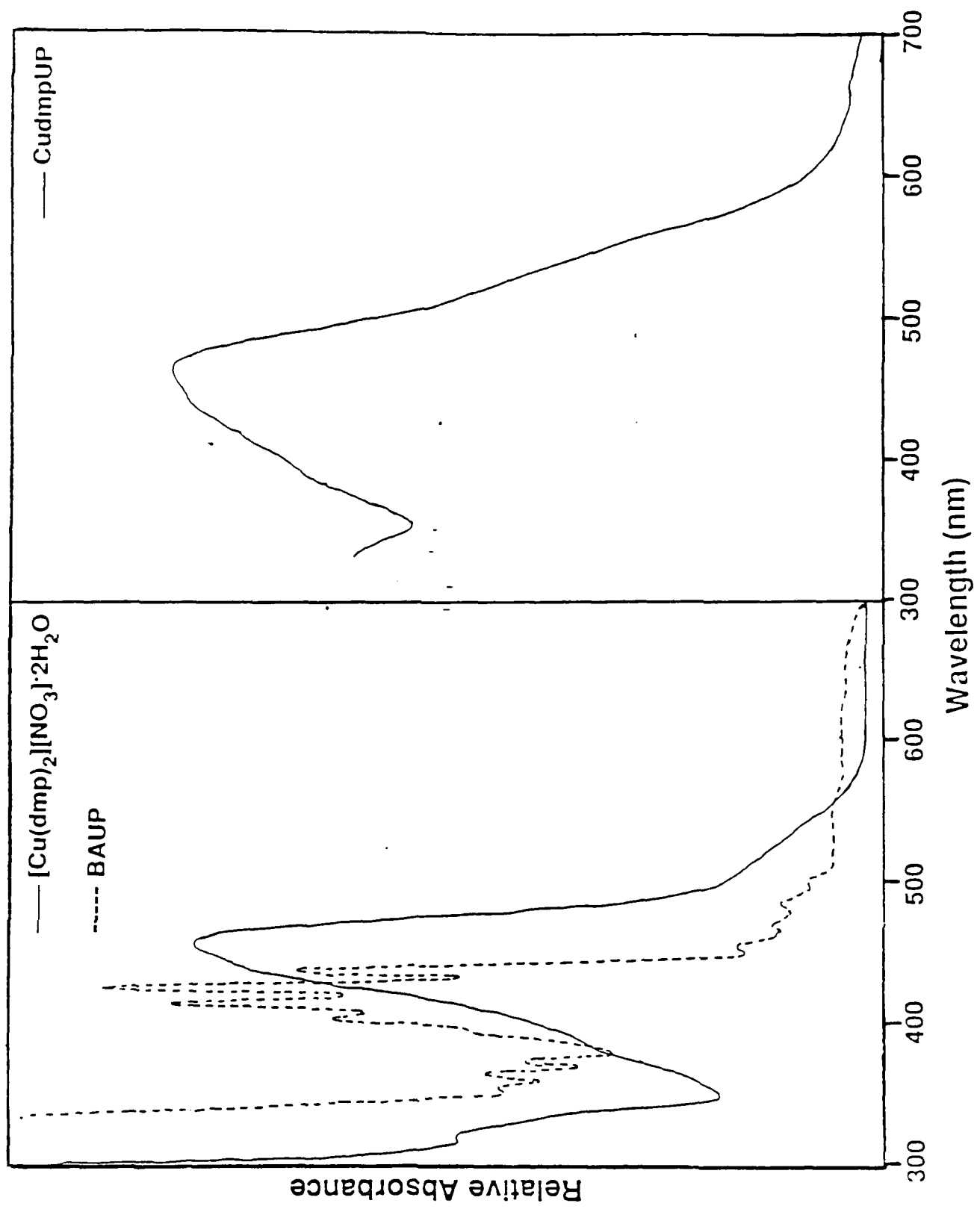
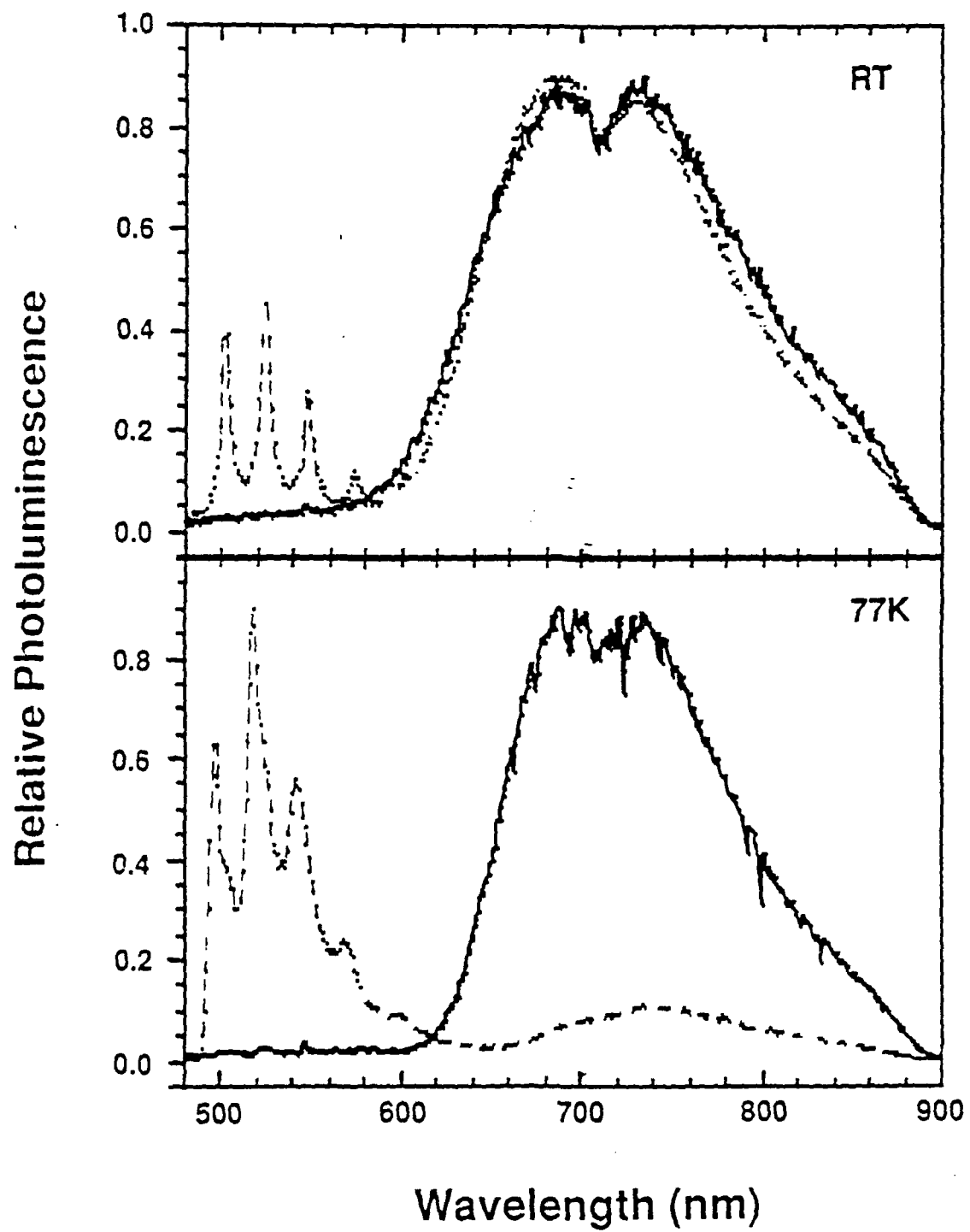


Fig 5



F₃C

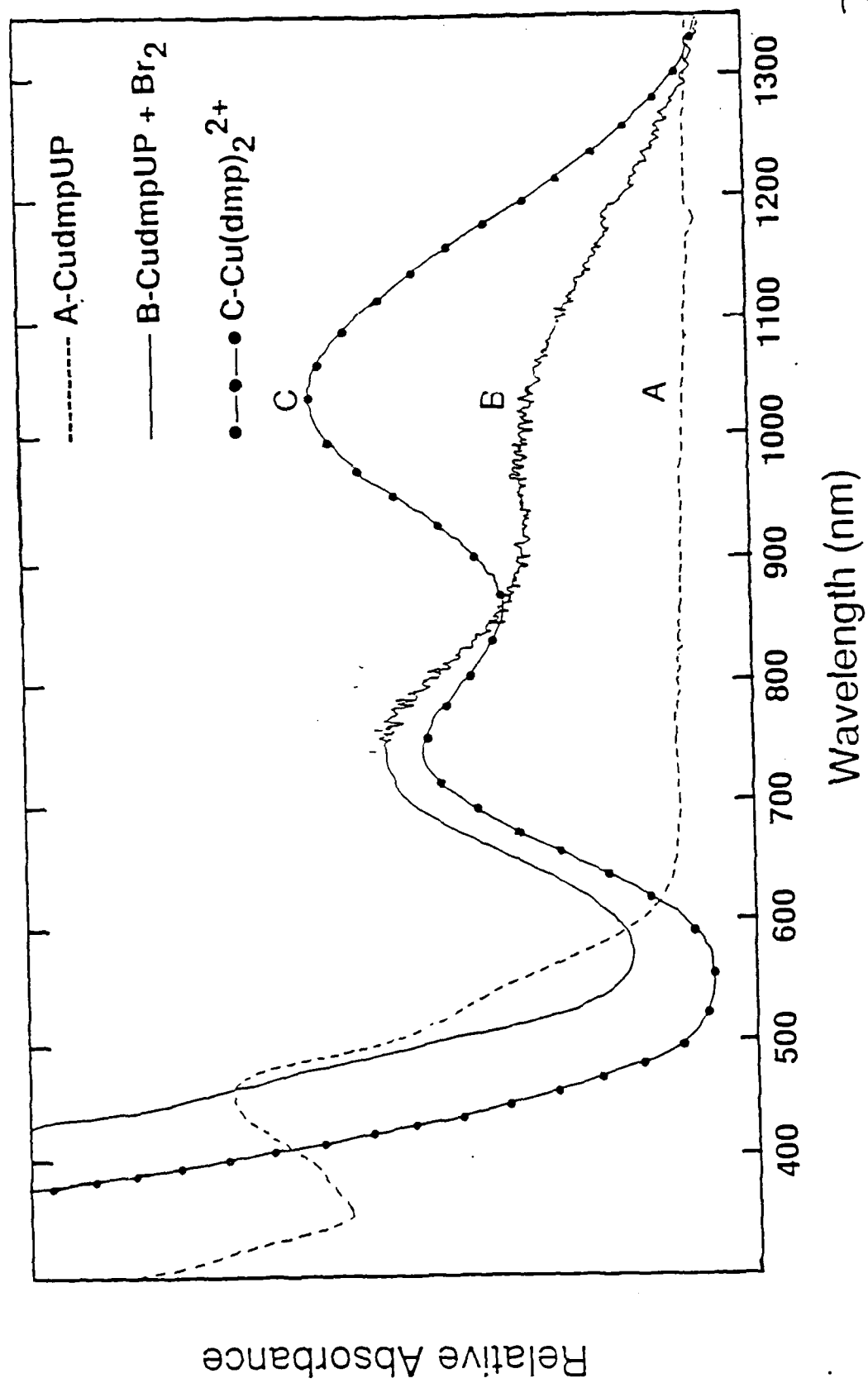
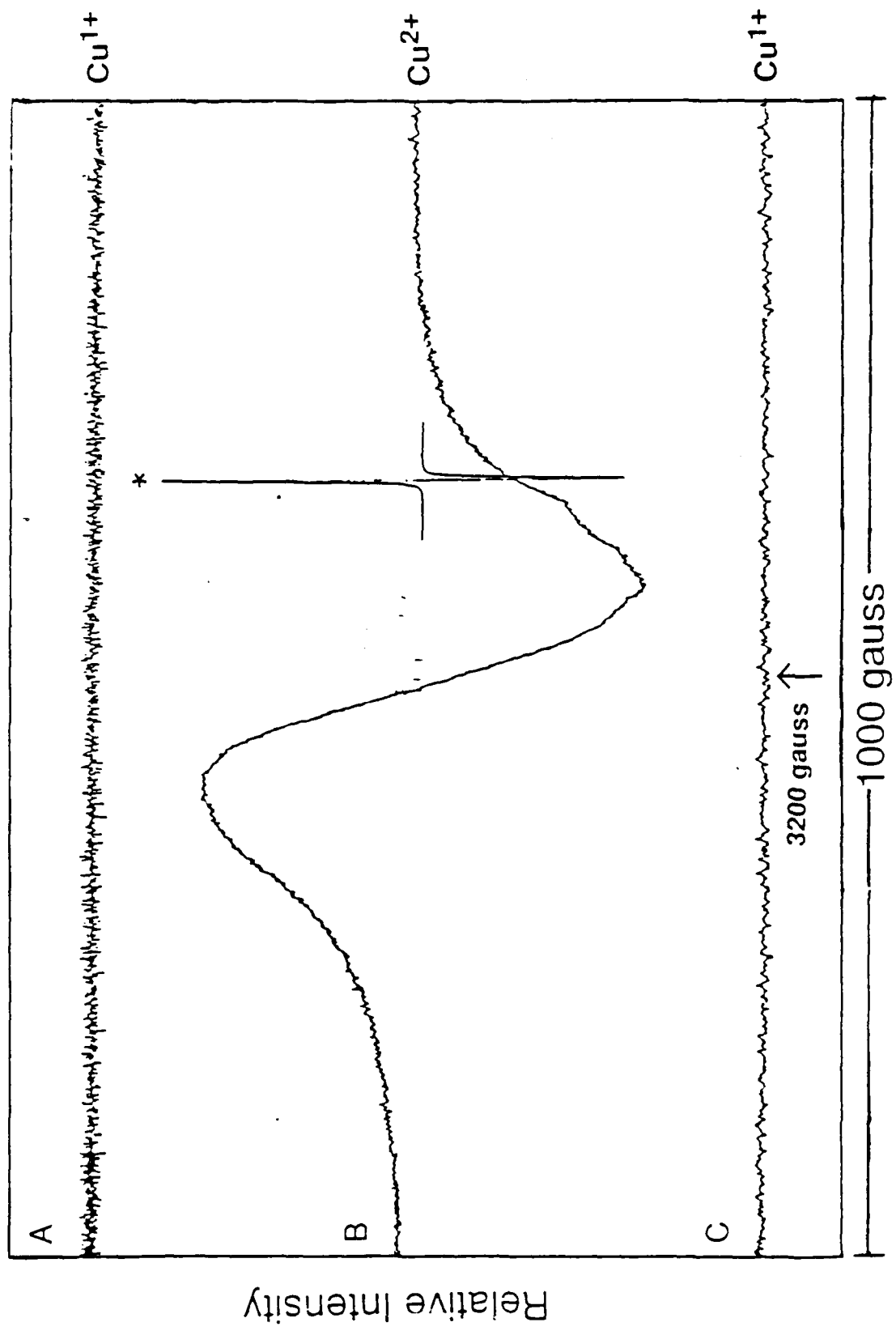


Fig 7





$1/d_{\text{obs}}^2$	$1/d_{\text{calc}}^2$	I_{rel}	h	l	k
0.0034	0.0035	100	0	0	2
0.0139	0.0139	41	0	0	4
0.0241	0.0240	3	1	0	2
0.0313	0.0312	14	0	0	6
0.0414	0.0411	19	1	1	0
0.0447	0.0446	10	1	1	2
0.0486	0.0489	11	1	1	3
0.0553	0.0554	9	0	0	8
0.0829	0.0831	33	2	0	1
0.0898	0.0900	16	2	0	3
0.1033	0.1037	8	2	1	1
0.1646	0.1645	4	2	2	0
0.1666	0.1669	5	1	0	13



$1/d^2_{\text{obs}}$	$1/d^2_{\text{calc}}$	I_{rel}	h	l	k
0.0035	0.0035	100	0	0	2
0.0142	0.0141	38	0	0	4
0.0275	0.0274	1	1	0	3
0.0318	0.0318	11	0	0	6
0.0388	0.0388	4	1	1	0
0.0565	0.0565	3	0	0	8
0.0700	0.0706	3	1	1	6
0.0782	0.0785	16	2	0	1
0.0854	0.0856	8	2	0	3
0.1005	0.1005	9	2	1	2
0.1554	0.1552	2	2	2	0
0.1581	0.1588	1	2	2	2
0.1691	0.1694	2	2	2	4
0.1869	0.1870	1	2	2	6
0.1944	0.1940	2	3	1	0

[Cu(dmp)₂]_{0.17}[BA]_{0.83}UAs - Fully Hydrated

$1/d^2_{\text{obs}}$	$1/d^2_{\text{calc}}$	I_{rel}	h	l	k
0.0027	0.0026	100	0	0	2
0.0107	0.0105	30	0	0	4
0.0238	0.0236	9	0	0	6
0.0419	0.0419	2	0	0	8
0.0609	0.0610	1	1	1	6
0.0652	0.0655	1	0	0	10
0.0775	0.0774	1	2	0	2
0.0795	0.0793	1	1	1	8
0.0842	0.0842	1	1	0	10
0.1129	0.1130	1	1	0	12
0.1469	0.1471	1	1	0	14



1/d²_{obs}	1/d²_{calc}	I_{rel}	h	l	k
0.0025	0.0025	100	0	0	2
0.0100	0.0100	71	0	0	4
0.0304	0.0304	9	1	0	4
0.0410	0.0407	49	1	1	0
0.0430	0.0429	31	1	0	6
0.0604	0.0604	11	1	0	8
0.0820	0.0821	60	2	0	1
0.0840	0.0839	46	2	0	2
0.0909	0.0914	17	1	1	9
0.1643	0.1644	11	2	1	10
0.2054	0.2058	20	3	0	6

[Cu(bcp)₂]_{0.21}[BA]_{0.79}UP - Fully Hydrated

$1/d^2_{\text{obs}}$	$1/d^2_{\text{calc}}$	I_{rel}	h	l	k
0.0020	0.0019	75	0	0	2
0.0079	0.0077	100	0	0	4
0.0173	0.0172	15	0	0	6
0.0306	0.0306	9	0	0	8
0.0412	0.0413	6	1	1	1
0.0478	0.0478	4	0	0	10
0.0821	0.0820	12	2	0	1
0.1635	0.1636	3	2	2	1



$1/d^2_{\text{obs}}$	$1/d^2_{\text{calc}}$	I_{rel}	h	l	k
0.0026	0.0026	100	0	0	2
0.0105	0.0105	71	0	0	4
0.0237	0.0237	20	0	0	6
0.0388	0.0385	32	1	1	0
0.0776	0.0777	85	2	0	1
0.0798	0.0796	48	2	0	2
0.1553	0.1547	27	2	2	1
0.1600	0.1599	12	2	2	3
0.1937	0.1932	19	3	1	1

[Cu(bcp)₂]_{0.18}[BA]_{0.82}UAs - Fully Hydrated

$1/d^2_{\text{obs}}$	$1/d^2_{\text{calc}}$	I_{rel}	h	l	k
0.0074	0.0073	100	0	0	4
0.0163	0.0163	18	0	0	6
0.0290	0.0290	8	0	0	8
0.0353	0.0353	1	1	0	6
0.0390	0.0384	1	1	1	1
0.0449	0.0452	1	1	1	4
0.0494	0.0493	1	1	1	5
0.0776	0.0777	4	2	0	2
0.0789	0.0800	3	2	0	3

BAUP

$1/d^2_{\text{obs}}$	$1/d^2_{\text{calc}}$	l_{rel}	h	l	k
0.0045	0.0047	100	0	0	2
0.0187	0.0187	7	0	0	4
0.0421	0.0421	33	1	1	1
0.0515	0.0515	15	1	1	3
0.0819	0.0819	31	2	0	0
0.0866	0.0866	29	2	0	2
0.0932	0.0925	2	2	0	3
0.1133	0.1130	2	2	1	3
0.1639	0.1639	7	2	2	0
0.1686	0.1686	7	0	0	12
0.1834	0.1827	2	1	1	11
0.2059	0.2060	18	3	1	1
0.2153	0.2154	7	3	1	3
0.3278	0.3278	4	4	0	0
0.3321	0.3319	4	2	1	14
0.4097	0.4097	4	4	2	0
0.4139	0.4139	4	3	0	14

BAUAs

$1/d^2_{\text{obs}}$	$1/d^2_{\text{calc}}$	l_{rel}	h	l	k
0.0042	0.0041	100	0	0	2
0.0167	0.0167	16	0	0	4
0.0236	0.0235	1	1	0	2
0.0288	0.0288	2	1	0	3
0.0375	0.0376	6	0	0	6
0.0398	0.0398	11	1	1	1
0.0455	0.0456	4	1	0	5
0.0482	0.0481	6	1	1	3
0.0569	0.0568	2	1	0	6
0.0775	0.0777	17	2	0	0
0.0817	0.0815	21	2	0	2
0.0942	0.0941	6	2	0	4
0.1151	0.1152	2	2	0	6
0.1551	0.1551	5	2	2	0
0.1592	0.1592	4	2	2	2
0.1718	0.1717	1	2	2	4
0.1949	0.1950	4	3	1	1
0.2032	0.2032	2	3	1	3
0.3112	0.3112	2	4	0	1
0.3195	0.3197	2	4	0	3
0.3489	0.3491	1	3	3	0
0.3500	0.3502	1	3	3	1
0.3887	0.3885	3	4	2	1